



Department of Chemistry

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NASA - Annual Report for 1996

This report summarizes progress during 1996 in our research effort entitled "New Fluorinated Polymers" (NAG 1-631), along with a description of additional results associated with a TAG supplement to this grant (items 2 and 5 below). Progress is reported in five areas:

1. Polyamides Derived from $(p\text{-HOOC}_6\text{H}_4)_2\text{C}(\text{CF}_3)\text{X}$ ($\text{X} = -\text{CF}_3, \text{OCH}_3, \text{Cl}$)
2. Phosphorus-containing "12F-PEK" - Effect of Systematic Replacement of $(p\text{-FC}_6\text{H}_4\text{COC}_6\text{H}_4)_2\text{C}(\text{CF}_3)_2$ Monomer by $(p\text{-FC}_6\text{H}_4)_2(\text{C}_6\text{H}_5)\text{PO}$
3. Poly(ether ketone)s Derived from $(p\text{-FC}_6\text{H}_4\text{COC}_6\text{H}_4)_2(\text{C}_6\text{H}_5)\text{PO}$
4. New CF_3 -containing Organosilane Monomers
5. New Monomers for 12F-PEK Analogues with Improved Processability and Solubility

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1. Polyamides Derived from (p-HOOC₆H₄)₂C(CF₃)X (X = -CF₃, OCH₃, Cl)

Five series of new polyamides (three, aromatic and two, aliphatic) have been prepared and characterized. This work was undertaken to determine if less expensive alternatives to the hexafluoroisopropylidene (6F) group could be found which not only would retain its excellent properties but which might also possess a backbone site for eventual crosslinking. To this end, three new trifluoroethylidene-linked aromatic dicarboxylic acids, in which one of the trifluoromethyl groups of the 6F linkage has been replaced by a hydroxyl, (3FOH), methoxy (3FM) or chloro group, have been prepared and characterized (Figure 1). At this time we also report the synthesis and characterization of twelve new aromatic polyamides derived from 3FM and 3FCI which are compared to their 6F analogs. In addition, four aliphatic polyamide derivatives of 3FM are also reported and compared to 6F analogues.

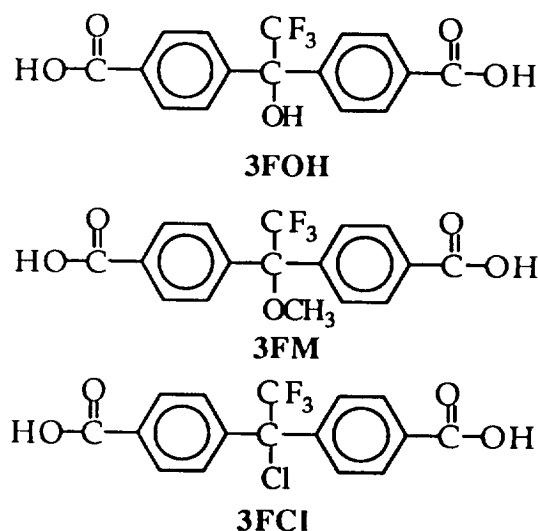


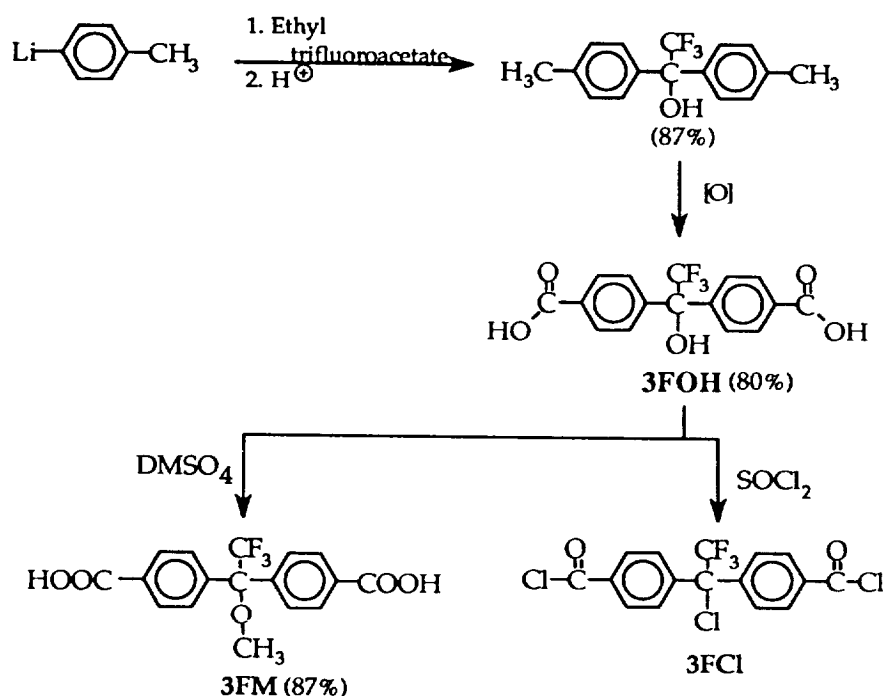
Figure 1 New CF₃-containing Diacids

Monomer Syntheses (Scheme 1)

Two monomers, 3FM and 3FCI, were prepared from the 3FOH monomer. The first monomer was prepared through methylation of the hydroxyl group by treating a basic solution of the 3FOH diacid with excess dimethyl sulfate.

The 3FM diacid was reacted with thionyl chloride along with a catalytic amount of DMF, to give a very viscous liquid product, 1-methoxy-1,1-bis(p-chloroformylphenyl)-2,2,2-trifluoroethane (3FMCl). Several unsuccessful attempts were made to crystallize from hexane, benzene and chloroform/toluene. Further purification was performed by distilling the product under high vacuum, although it remained a highly viscous liquid on cooling.

The 3FCl diacid chloride, prepared by reacting 3FOH diacid with thionyl chloride, yielded a single product, 3FCl diacid chloride. Like 3FMCl, 3FCl diacid chloride is also a very viscous liquid.

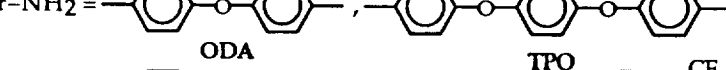


Scheme 1 Synthesis of 3FOH, 3FM and 3FCl Monomers

Polyamides

All polyamides prepared in this study are soluble in NMP, DMAc, DMSO, THF, and pyridine. In order to evaluate the effect of substituting a methoxy or chloro group for one of the trifluoromethyl groups of the hexafluoroisopropylidene unit, the properties of a 3FM and 3FCl polyamide series derived from six aromatic diamines were compared to an analogous 6F series. All of the aromatic diamine-based polyamides were found to be amorphous as determined by

Diamines (Ar)	% Polymer Yield			Viscosity ^a η_{inh} dL/g		
	3FM	6F	3FCI	3FM	6F	3FCI
ODA	88	94	87	0.36	1.32	0.41
TPQ	92	93	96	0.39	1.16	0.41
BAPB	89	94	93	0.46	0.94	0.34
BDAF	95	95	96	0.41	1.02	0.49
6F Diamine	90	94	83	0.32	0.71	0.27
ABL	62	92	57	0.35	1.52	1.08

$\text{H}_2\text{N}-\text{Ar}-\text{NH}_2 =$


which were, respectively, 62 and 57 percent. The inherent viscosities of the 3FM and 3FCI polyamides ranged between 0.27 and 0.49 dL/g (with the exception of the 3FCI-ABL polyamide at 1.08 dL/g) while the 6F polyamides exhibited much higher viscosities (0.71 and 1.52 dL/g). Viscosity data for C₃ - C₆ aliphatic polyamides are found in Table 3, and in each case the inherent viscosity of the 3FM series is also significantly lower than in the 6F series. The lower viscosities of all the 3FM or 3FCI series can possibly be attributed to traces of impurity in the 3FMCI and 3FCI diacid chlorides which were prepared from purified diacids and then used directly in the polymerizations without additional purification. Nevertheless, all of the polyamides (from 3FM, 3FCI and 6F diacids) formed tough, transparent and creasable films from DMAc.

Table 2 Properties of the Polyamides Synthesized from 3FM or 3 FCI or 6F and Aromatic Diamines

Diamines (Ar)	Glass Transition Temperature ^a (°C)			TGA 10% Weight Loss ^b (°C)			% Char Yield			Dielectric Constants	
	3FM	6F	3FCI	3FM	6F	3FCI	3FM	6F	3FCI	3FM	6F
ODA	272	305	301	471	500	425	49	45	48	2.73	2.99
TPQ	238	276	276	479	509	419	47	47	51	—	—
BAPB	254	284	272	483	518	447	52	50	52	2.88	2.95
BDAF	250	262	274	491	517	504	51	44	50	2.64	2.70
6F Diamine	278	314	317	462	507	449	38	38	43	—	—
ABL	311	337	ND ^c	471	500	457	46	34	41	2.80	2.68

a: DSC, 20°C/min.

b: 20°C/min., N₂ atm.

c: ND = not detectable

The 10% weight loss temperature of the TGA was taken as the reference point for comparing the thermal stability of each polyamide; the values ranged from 462 to 491 °C, from 419 to 504 °C, and from 500 to 518 °C for the 3FM, 3FCI and 6F aromatic series, respectively (Table 2). In general, the thermal stability of the aromatic polyamides falls in the order 6F > 3FM > 3FCI; however, with the diamine BDAF the order is 6F > 3FCI > 3FM. Generally, the thermal stability of the 6F series is about 30 - 40° greater than the 3FM series, while the 3FCI is generally significantly lower still. The origin of the excellent thermal stability of the 3FCI-BDAF polymer is not clear at this time. Thermal stabilities of the aliphatic diamine-based polyamides ranged from 370 to 437 ° for the 3FM-derived series and from 423 - 457 ° for the analogous 6F series (Table 3).

Table 3 Properties of the Polyamides Synthesized from 3FM, or 6F and Aliphatic Diamines

Diamines (Ar)	η_{inh}^a (dL/g)		T_g^b (°C)		TGA ^c (°C)	
	3FM	6F	3FM	6F	3FM	6F
-(CH ₂) ₃ -	0.79	1.03	177	218	370	423
-(CH ₂) ₄ -	0.61	0.95	175	175	383	457
-(CH ₂) ₅ -	0.70	0.93	ND	ND	370	453
-(CH ₂) ₆ -	0.77	0.90	165	184	437	453

a: measured in NMP @25°C; b: measured by DSC;
c: 10% weight loss, 20°/min., N₂ atm.

The greater thermal stability of the 6F series over either the 3FM or 3FCI series is probably due to the well-documented higher thermal stability of the CF₃ group compared to the methoxy or chloro group. However, even though the 6F polyamides are more thermally stable than the 3FM aromatic polyamides when determined at 10% weight loss, the percent char yields for the

3FM (or 3FCI) series are equal to or greater than the char yields for the 6F series when measured at 1000 °C.

Figure 2 shows a TGA (in nitrogen) overlay trace of the 3FM-BDAF, 3FCI-BDAF and 6F-BDAF polyamides. It is observed that the 3FM and 3FCI polyamides decomposed by a two-stage decomposition process whereas the 6F polyamide decomposed by a one-stage process. The more pronounced two-stage decomposition trace of the 3FCI-BDAF polyamide displays an earlier onset for its first decomposition stage, and thus a lower “10 percent weight loss thermal stability,” but still results in a char yield greater than that for the 6F-BDAF polyamide. The two-stage decompositions and slightly higher char yields of the 3FM and 3FCI polyamides can possibly be attributed to thermal cross-linking and the formation of a slightly more stable intermediate in the thermal decomposition mechanism.

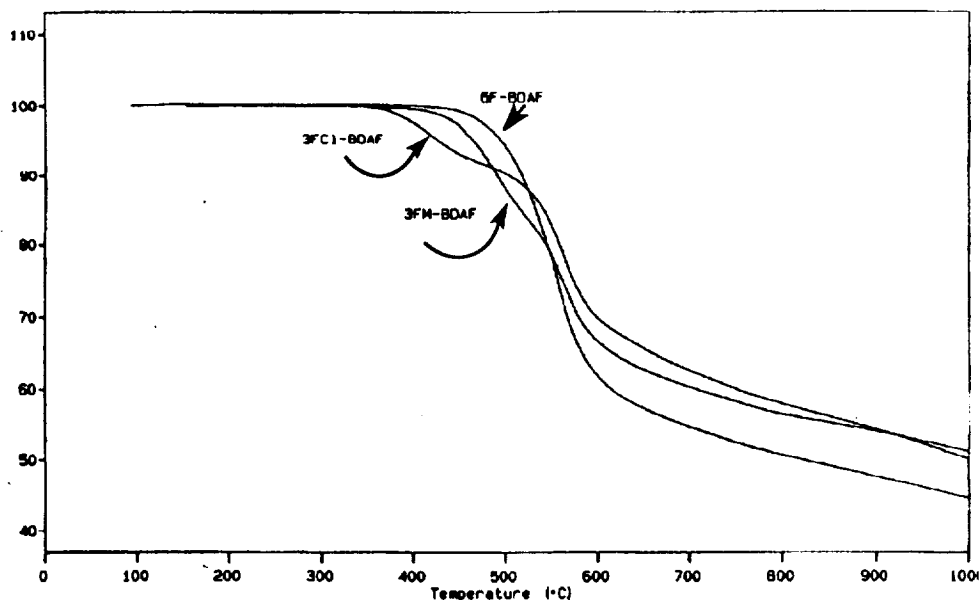


Figure 2: TGA Trace of 3FM-BDAF, 6F-BDAF and 3FCI-BDAF

Glass transitions for the 3FM aromatic polyamide series ranged from 238° to 311°C and those of the 3FCI series ranged from 272° to 317°C, (T_g not observed for 3FCI-ABL polymer). The T_g values of the analogous 6F series ranged from 262° to 337°C (see Table 2). The T_g values for the 3FCI polyamides average 30 °C higher than those for the 3FM polyamides and are very close

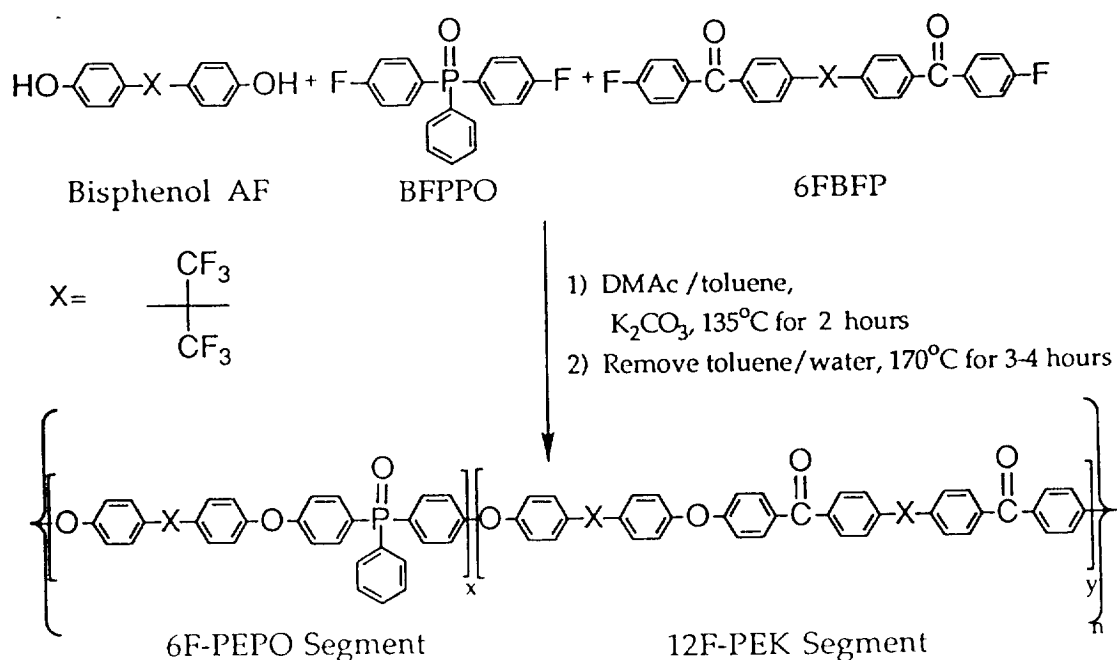
to the analogous 6F polyamide values. The values for aliphatic series of 3FM polyamides ranged from 165 to 177 °C, whereas the analogous 6F polymers have values ranging from 175 to 218 °C (Table 3).

Table 2 also lists the dielectric constants of four of the 3FM polyamides and their 6F analogs. Interestingly, the 3FM polyamides had lower values than the 6F analogues for the ODA, BAPB- and BDAF-containing polymers.

2. Phosphorus-containing "12F-PEK" - Effect of Systemtic Replacement of (p-FC₆H₄COC₆H₄)₂C(CF₃)₂ Monomer by (p-FC₆H₄)₂(C₆H₅)PO

In order to improve the resistance of "12F-PEK" to atomic oxygen ablation, without adversely affecting its otherwise excellent properties (good solubility, excellent optical transmission, high thermal stability and low dielectric constant), we have prepared and evaluated (with the assistance of the NASA-Langley sponsors) a series of phosphorus-containing 12F-PEK Copolymers (6F-PEPO/12F-PEK Random Copolymers).

Random copolymers of Bis AF and varying BFPPPO/6FBFP mole percent ratios were synthesized in 50-70% yield using a standard Williamson synthesis technique (Scheme 2). The modified 12F-PEK series polymers are colorless, and are easily soluble in common organic solvents from which strong, transparent, creasable films can be obtained.



Scheme 2 Williamson Synthesis of 6F PEPO/12-F PEK Random Copolymer Series

Table 4 lists inherent viscosity, Tg, TGA, dielectric constant and water contact angle data for the 6F-PEPO/12-F PEK copolymer series. The polymers showed inherent viscosities, which were measured in filtered chloroform at 25°C, which ranged from 0.63 - 0.92 dL/g corresponding to molecular weights of approximately 200,000 as determined by GPC analysis run in filtered THF with polystyrene standards. None of the polymers exhibited a Tm by DSC. It is noted that the incorporation of the phosphorus monomer, BFPPO, into the 12F-PEK may cause a very slight increase in Tg; however, solubility, thermal stability and most importantly, dielectric constant remain excellent in the series. The dielectric constant remains below 2.5 up to fifty percent incorporation of BFPPO.

Table 4 Properties of 6F PEPO/12F-PEK Copolymers

Composition (Mol% BFPPO:6FBFP)	Inherent Viscosity dL/g ^a	TGA ^b Air	Tg ^c °C)	Dielectric Constant @10Ghz	Water Contact Angle
0:100	0.86	487	173	2.43	101 ± 2
25:75	0.78	502	185	2.43	102 ± 1
50:50	0.92	489	188	2.49	100 ± 1
75:25	0.85	497	184	2.55	99 ± 1
90:10	0.63	536 ^d	212 ^d	2.60	96 ± 1

a: measured in Chloroform; b: 10% weight loss; c: by DSC; d: measured on Rheometrics STA-1000 instrument, others on Seiko (NASA Langley)

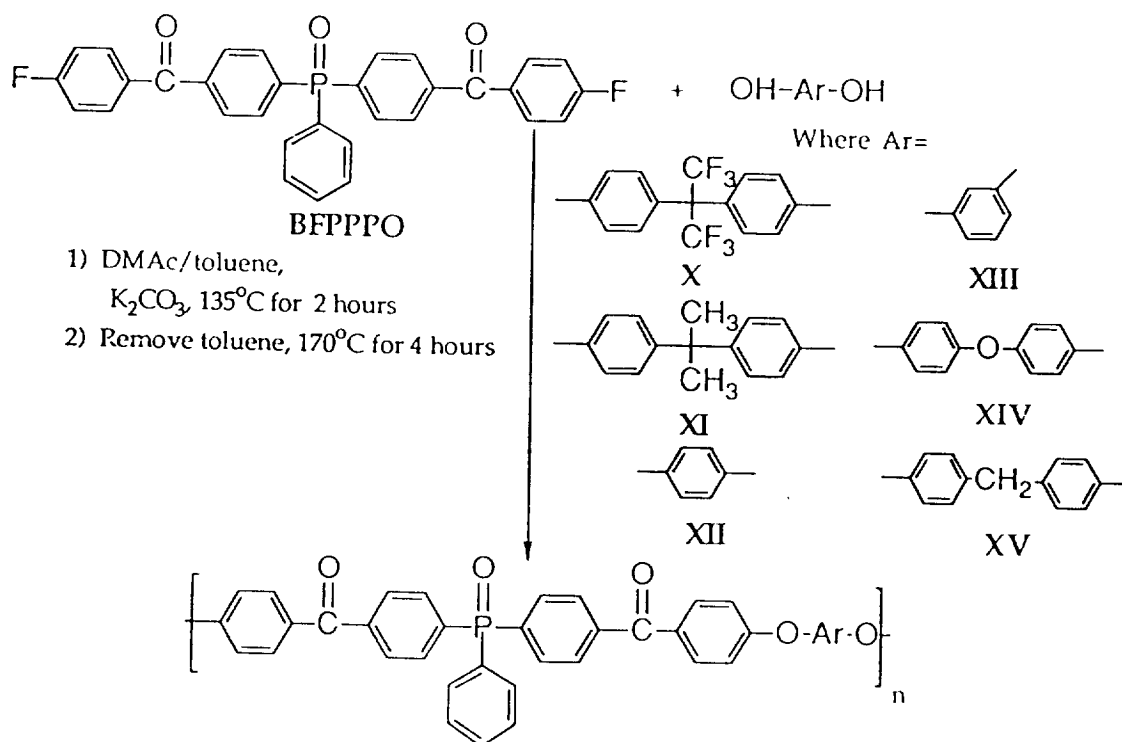
Resistance to atomic oxygen ablation also appears to be considerably improved by phosphorus incorporation. Although the results are sketchy, incorporation of the BFPPO monomer into the 12F-PEK backbone reduced the mass loss on exposure to atomic oxygen from 45 - 50% for either a 12F-PEK standard, or a Kapton standard, to *ca.* 17% for the 25:75 mol % 6F PEPO/12F-PEK copolymer (Table 5). However, fogging of all of the films of 6F PEPO/12F-PEK polymer compositions appears to have significantly reduced their transmission at 500 nm, an effect not seen with the 12F-PEK control. Ultraviolet cutoffs were not significantly changed by the exposure (Table 5).

Table 5: Modified PEK Films Before and After Exposure to Atomic Oxygen

Composition (Mol % BFPPO: 6FBFP - %P)	%Transmission (@ 500 nm)		UV Cutoff (Nm)		Film Weight (g)		%Weight Lost
	Before	After	Before	After	Before	After	
0:100 (12F - PEK CONTROL)	90	- ^a	372	- ^a	-	-	-
RERUN	89	87.5	372	364	0.0784	0.0435	44.5
25:75 1% P	84	39	363	344	-	-	-
RERUN	84	48	363	364	0.0834	0.0692	17
50:50 2.1% P	79	32	355	348	-	-	-
75:25 3.5% P	81	55	366	325	-	-	-
KAPTON (1 mil)	77	57.4	466	448	0.0697	0.0371	47

^a Approximately 85% of film destroyed in experiment

Copolymers of BFPPO and six bisphenols were synthesized in greater than 90% yield using standard Williamson synthesis techniques (Scheme 3). The poly(ether ketone-phosphine oxide)s (PEK-PO's) were slightly off-white and are easily soluble in common organic solvents such as chloroform, THF, acetone, etc. Strong, transparent, creasable films are readily obtained.



Scheme 3. Williamson Synthesis of Bis[4-(4-fluorophenoxy)phenyl]-phenylphosphine Oxide (BFPPPO) and Six Bisphenols.

Table 6 summarizes the inherent viscosity, T_g, TGA, char yield, and contact angle data for the PEK-PO's. Inherent viscosities, measured in filtered chloroform at 25 °C, ranged from 0.76 dL/g for XI to 1.32 dL/g for XIII. None of the polymers exhibited a T_m by DSC. Glass transitions were all near 200 °C, ranging from 195 °C for XI, VI, and XV to 207 °C for X and XII. Insertion of the phenyl-ketone group to the triphenylphosphine oxide moiety, bis(fluorophenyl)phenyl phosphine oxide (BFPPPO), by copolymerization of BFPPPO and either Bis A or hydroquinone slightly decreases the T_g from 205 °C for the copolymer with Bis A and BFPPPO [Smith, *et al.*, *Polym. Mater. Sci. Eng. Prepr.*, 65, 108 (1991)] to 195 °C for the copolymer with Bis A and BFPPPO, and from 215 °C for the copolymer with hydroquinone and BFPPPO (Smith, *et al.*) to 207 °C for the copolymer with hydroquinone and BFPPPO.

All polymers exhibited excellent thermal stability (measured by TGA) ranging from 528 °C for XI to 549 °C for XII and XIV in nitrogen at a 10% weight loss, and from 513 °C for XIII to 545 °C for XII in air at a 10% weight loss. TGA 5% weight loss thermal stabilities for copolymers of BFPPPO with Bis A or hydroquinone have been reported as 490 °C and 520 °C, respectively, in air (Smith, *et al.*). The decomposition of this series of copolymers in nitrogen involves a single step, leaving substantial amounts of char yields ranging from 38 to 58% for XI and X, respectively, possibly due to the fact that phosphorus-containing degradation products for the most part are non-volatile. Similar high char yields for copolymers of BFPPPO with Bis A or hydroquinone have been reported as 31 and 50% (Smith, *et al.*), respectively, at 600 °C. A two-step decomposition by TGA measurement (conducted in air) was observed for all polymers. Water contact angles were measured on films cast from chloroform and ranged from 78 ° for XII to 84 ° for XIII, suggesting rather high dielectric constants for this polymer series.

Table 6. Inherent Viscosity, Tg, TGA, Char Yield and Water Contact Angle Data for Copolymers with Bis[4-(4-fluorophenoxy)-phenyl]phenylphosphine Oxide (BFPPPO and Six Bisphenols

Polymer	η_{inh} (CHCl ₃) (dL/g)	T _g by DSC ^a (°C)	TGA ^b N ₂ (°C)	TGA ^b Air (°C)	Char Yields at 700°C (%)	Water Contact Angle
PEKPO/Bis AF (X)	0.80	207	538	533	58	83°
PEKPO/Bis A (XI)	0.76	195	528	528	38	79°
PEKPO/ Hydroquinone (XII)	1.24	207	549	545	43	78°
PEKPO/ Resorcinol (XIII)	1.32	201	532	513	50	84°
PEKPO/ Oxydiphenol (XIV)	0.77	195	549	532	57	82°
PEKPO/ Methane- diphenol (XV)	1.10	195	534	526	52	81°

^a measured on a Rheometrics STA-1000 instrument; ^b 10% weight loss, measured on a Rheometrics STA-1000 instrument at 20°C/min

Table 7 summarizes the UV-Vis spectral data for the PEKPO's. In order to obtain UV-Vis data, each polymer had to be diluted to about 2.0×10^{-2} g/L in chloroform. The wavelength of maximum absorbance (λ_{max}) ranged from 290 nm for 12F-PEK to 299 nm for XI, XII, and XV. Absorbivity at (λ_{max}) ranged from 45 L g⁻¹cm⁻¹ for XV to 66 L g⁻¹cm⁻¹ for XII. The polymer (X) that substitutes the phenylphosphine oxide group for one of the 6F groups of 12F-PEK has a lower absorbivity at (λ_{max}) than 12F-PEK itself. Absorbivity at $\lambda=315$ nm ranged from 14 L g⁻¹cm⁻¹ for 12F-PEK to 40 L g⁻¹cm⁻¹ for XI and XII. The polymer (X) that substitutes the phenylphosphine oxide for the 6F groups in the 6FBFP monomer has a slightly higher

absorbivity at $\lambda=315$ nm than the pure 12F-PEK material. The absorbivity at $\lambda=315$ nm can be used as a measurement of the UV tailing into the visible region which results in the pale tan color of the polymers. In other words, the higher the absorbivity at $\lambda=315$ nm, the more off-white the polymers become. Therefore, the UV-Vis data collected are consistent with the observation that 12F-PEK is virtually colorless, polymer X is slightly off-white and polymers XI-XV are slightly more off-white, with XI and XII having the most color.

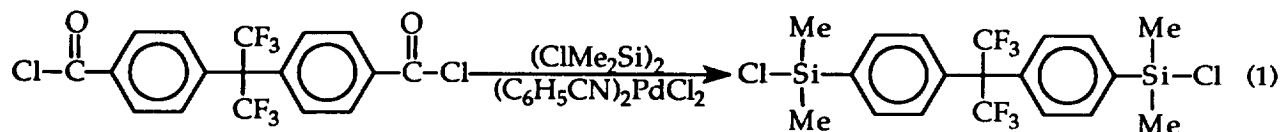
Table 7. UV-Vis Data for 12F-PEK, and Copolymers with Bis[4-(4-fluorophenoxy)phenyl]-phenylphosphine Oxide (BFPPPO) and Six Bisphenols.

Polymer	Conc. of polymer (c) (g/L)	Max. Absorbance (A)	Wave-length of Max. Absorbance (λ_{max} nm)	Absorb-tivity at λ_{max} ^a L g ⁻¹ cm ⁻¹	Absorb-tivity at $\lambda=315$ nm ^a L g ⁻¹ cm ⁻¹
12F-PEK	2.2×10^{-2}	1.21	290	56	14
BFPPPO/Bis AF (X)	1.8×10^{-2}	0.83	294	45	17
BFPPPO/Bis A (XI)	1.8×10^{-2}	1.04	299	58	40
BFPPPO/Hydroquinone (XII)	2.2×10^{-2}	1.46	299	66	40
BFPPPO/Resorcinol (XIII)	2.0×10^{-2}	1.08	297	54	25
BFPPPO/Oxydiphenol (XIV)	2.2×10^{-2}	1.28	298	58	35
BFPPPO/Methane-diphenol (XV)	2.0×10^{-2}	1.03	299	52	32

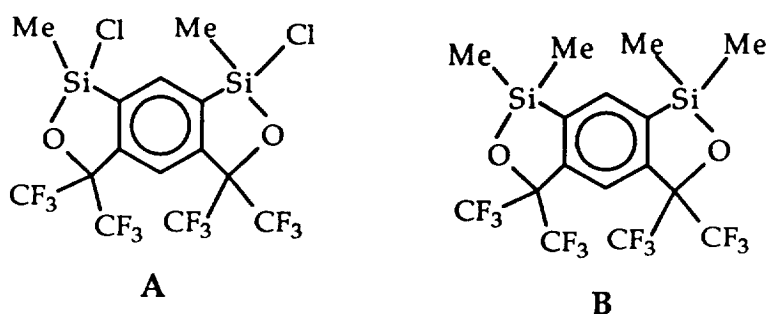
^a Calculated Using $A=abc$, Where: A=absorbance, $a=a^1$ =absorbivity, b=conc. of sample (g/L), c=cuvet length (cm)⁴⁷

4. New CF₃-Containing Organosilane Monomers

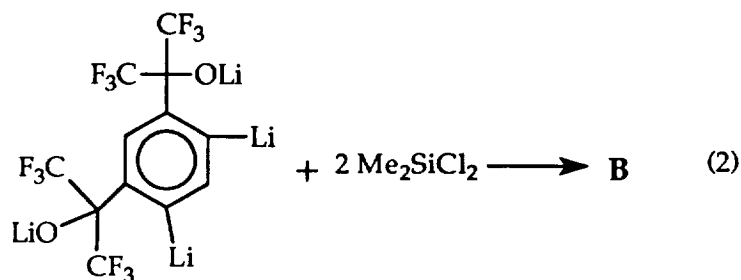
Results in the development of new CF₃-containing organosilane monomers remain somewhat elusive, although some progress can be reported. Repeated attempts to prepare 2,2-bis[(4-chlorodimethylsilyl)phenyl]hexafluoropropane (eq. 1) by the reported literature method



led to complex mixtures which could not be separated. The other target monomer (see A below)



proved equally frustrating. Although we have prepared and completely characterized B (eq. 2) (including an X-ray structure), A has not yet been isolated. The reason for this failure

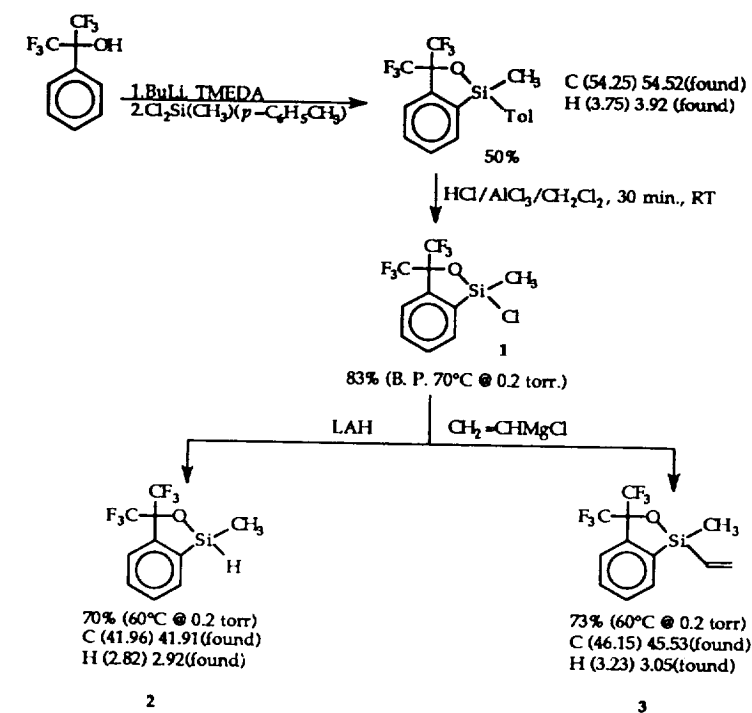


likely resides in the fact that the tetralithiated intermediate (see eq. 2) must be first reacted with the sterically demanding reagent, (p-CH₃C₆H₄)CH₃SiCl₂, to obtain the precursor to A (above) in which the p-tolyl groups replace the chlorine atoms. Work continues in this area, but not at a high priority.

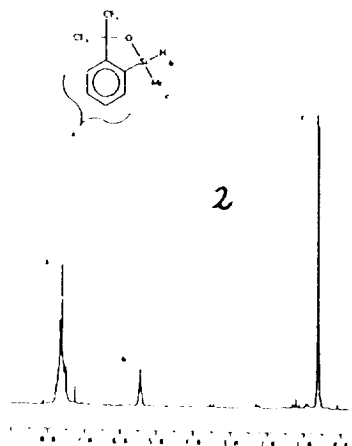
Better success has been realized with preparation of new silane-monomers derived from hexafluoro-2-phenyl-2-propanol. The outline shown below summarizes some of our recent results in this area.

New Silicon-containing Monomers Derived from Hexafluoro-2-phenyl-2-propanol

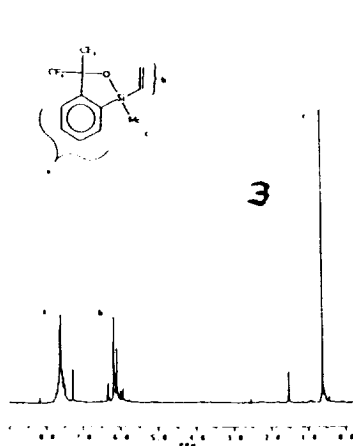
A. Silicon-functional 2-Oxa-1-silaindan Monomers



¹H NMR MethylHydro Derivative

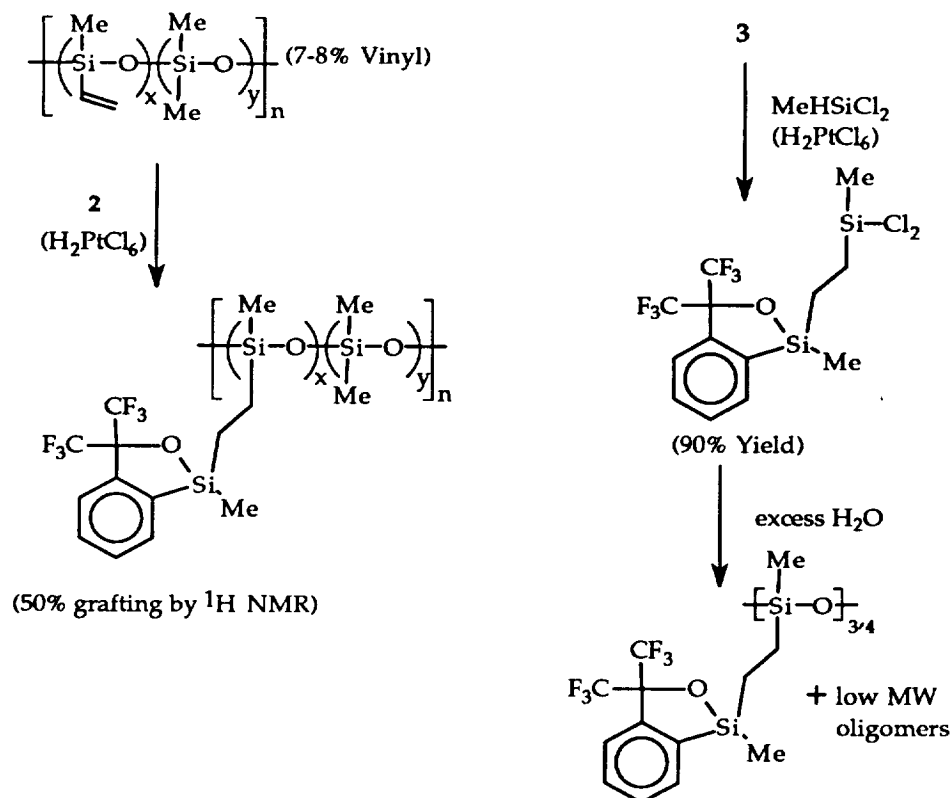


¹H NMR MethylVinyl Derivative



- Compounds 1-3 are new, silicon-functional synthons derived from 2-oxa-1-silaindan.

B. Preliminary Results - Polymers/Oligomers



5. New Monomers for 12F-PEK Analogues with Improved Processability and Solubility

This work is directed toward finding modified 12F-PEK backbone structures having improved properties, especially solubility in non-aggressive solvents. To this end, the 12F-PEK monomer, bis-AF has been targeted for modification.

A literature search has found a patented procedure for condensing phenol into methyl ketones in the presence of mercaptoacetic acid (eq. 3). Using this procedure, we have prepared



bisphenols, bis- C_{11} and bis- C_{17} in which R is respectively a C_{11} or C_{17} aliphatic chain, in good yield ($\sim 80\%$). Preliminary experiments indicate that the preparation of the targeted 12F-PEK analogues occurs without complications.

1996 Publications and Presentations Acknowledging NASA Support

A. Publications (See attached)

David J. Irvin, Patrick E. Cassidy, David L. Meurer, John W. Fitch III, David A. Taylor, Anne St. Clair, and Diane Stoakley, "N-Methylated copoly(imide amide)s containing hexafluoroisopropylidene," *Polymer*, 37(11), pp. 2227-2232 (1996).

V. S. Reddy, Patrick E. Cassidy, John W. Fitch III, Brent D. Lunceford, and David Person, "Hexafluoroisopropoxy-containing polyesters," *Polymer* 37(21), pp. 4873-4875 (1996).

V. S. Reddy, W. J. Weikel, J. Arbaugh, John W. Fitch, and Patrick E. Cassidy, "Synthesis and characterization of new fluorinated polyacrylates: 2," *Polymer*, 37(20), pp. 4653-4656 (1996).

B. Presentations (See attached)

P. W. Youngman, J. W. Fitch, and P. E. Cassidy, "Synthesis and Characterization of Poly(ether ketone)s Containing Phosphorus and Fluorine," 211th ACS National Meeting, New Orleans, Louisiana, March 24-28, 1996.

P. E. Cassidy, J. W. Fitch, H. G. Boston, and V. S. Reddy, "A New Aromatic Diacid Containing the Trifluoromethyl Group and its Polymers," STEPI-4, Montpellier, France, May 13-15, 1996.

John W. Fitch, V. S. Reddy, Paul W. Youngman, Glenn A. Wohlfahrt and Patrick E. Cassidy, "Poly(phosphine oxide ether ketone)s Derived from Bis(4 carboxylphenyl)phenyl-phosphine oxide," 212th ACS National Meeting, Orlando, Florida, August 25-29, 1996.